

STOCHASTIC SCHEMES OF DIELECTRIC RELAXATION IN CORRELATED-CLUSTER SYSTEMS

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Abstract

Unlike the classical exponential relaxation law, the widely prevailing universal law with its fractional power-law dependence of susceptibility on frequency cannot be explained in the framework of any intuitively simple physical concept. The resulting constancy of the ratio of the imaginary to the real parts of the complex susceptibility, known as the “energy criterion”, has a pleasing simplicity but the understanding of its origins needs a special theoretical treatment. A fresh light on the stochastic nature of the dielectric relaxation has been shed by a novel stochastic approach introduced in the last decade. Since the theoretical analysis involved is rather unfamiliar, the aim of this paper is to give some useful comments and suggestions which should help to follow in details the proposed stochastic scheme of relaxation leading to the well-known empirical responses. We justify the universality of the power-law macroscopic response as well as Jonscher’s screening and energy criterion ideas, and we give a new basis to the research into the significance of relaxation processes.

Keywords: Dielectric relaxation; screening; energy criterion; heavy-tailed distribution.

1. Introduction.

Dielectric relaxation in solids, a process commonly defined as an approach to equilibrium of a dipolar system driven out of equilibrium by a step or alternating external electric field, represents one of the most intensively researched topics in experimental and theoretical physics, see e.g. [1-21]. Wide-ranging experimental information resulting from the studies of the basic dielectric characteristics (i.e., the time decay of the depolarization current $i(t)$ and the frequency-dependent complex dielectric permittivity $\epsilon(\omega)$ or susceptibility $\chi(\omega) \propto \epsilon(\omega) - \epsilon_\infty$, where ϵ_∞ is the asymptotic value of the dielectric permittivity $\epsilon(\omega)$ at high frequencies) has led to the conclusion that the classical phenomenology of relaxation breaks down in complex materials. It has been found that the Debye behaviour, represented by the exponentially decaying relaxation function

$$\phi(t) = \exp(-\omega_p t) \quad (1)$$

yielding

$$i(t) \propto f(t) = -\frac{d\phi(t)}{dt} = \omega_p \exp(-\omega_p t)$$

and

$$\chi(\omega) \propto \phi^*(\omega) = \int_0^\infty e^{-i\omega t} f(t) dt = \frac{1}{1 + i\omega/\omega_p} \quad (2)$$

(where the constant ω_p denotes the loss peak frequency) is hardly ever found in nature and that the deviations from it for many dielectrics may be relatively large [3, 10, 15]. A class of systems exhibiting the non-Debye relaxation patterns includes various complex materials such as supercooled liquids, amorphous semiconductors and insulators, polymers, disordered crystals, molecular solid solutions, glasses, etc.

For a long time effort was being diverted to a purely qualitative representation of the shape of the non-Debye dielectric functions $\phi(t)$ or $\phi^*(\omega)$ in terms of certain mathematical expressions without in any way going into the physical significance of these representations. It turns out that all dielectric data are characterised well enough by a few empirical functions [2, 3, 10, 15]. The time-domain relaxation data usually are fitted by means of the stretched exponential relaxation function

$$\phi(t) = \exp(-(\omega_p t)^\alpha) \quad \text{with } 0 < \alpha < 1 \quad (3)$$

known as the Kohlrausch-Williams-Watts (KWW) function and coincident with the Debye case (1) for $\alpha = 1$. The most popular analytical expression applied to the complex susceptibility data is given by the Havriliak-Negami (HN) function

$$\phi^*(\omega) = \frac{1}{(1 + (i\omega/\omega_p)^\alpha)^\gamma} \quad (4)$$

where $0 < \alpha, \gamma < 1$. For $\alpha = 1$ and $\gamma < 1$, formula (4) takes the form known as the Cole-Davidson (CD) function; for $\gamma = 1$ and $\alpha < 1$ it takes the form of the Cole-Cole (CC) function, and for $\alpha = 1$ and $\gamma = 1$ one obtains the classical Debye form (2).

We repeat that these various model functions are essentially attempts to characterise the observed behaviour without in any way indicating the physical mechanisms involved. To that extent, we note that the problem of understanding the nature of dielectric relaxation is as yet largely open since we do not have a sufficiently general method of approach to the relaxation processes. At the same time we note certain fundamental features of relaxation response which make it clear that we are faced with some very general processes into which we require a much deeper insight.

The HN, CC, CD, and KWW model functions all show the high-frequency limit of the response characterised by the fractional power law [2, 15]:

$$\chi'(\omega) = \tan\left(\frac{n\pi}{2}\right) \chi''(\omega) \propto \omega^{n-1} \quad \text{for some } 0 < n < 1 \quad (5)$$

which has the straightforward consequence of the constant ratio of the imaginary to the real components of the dielectric susceptibility $\chi(\omega) = \chi'(\omega) - i\chi''(\omega)$:

$$\frac{\chi''(\omega)}{\chi'(\omega)} = \cot\left(n\frac{\pi}{2}\right) \quad \text{for } \omega \gg \omega_p. \quad (6)$$

Let us note that this relation implies that the ratio of energy lost per radian to the energy stored at the peak is independent of frequency. This very simple and intuitively evident property is characteristic of the prevailing universal response of most dielectric materials. We call this the “energy criterion” and it is neither known nor predicted by any of the accepted theories of relaxation.

Important for our discussion of relaxation phenomena is the concept of residual loss [22] which remains after the removal of such strongly frequency-dependent processes as the direct-current contribution going as ω^{-1} , or low-frequency dispersion where loss is proportional to ω^{n-1} with $n \rightarrow 0$, or dipolar loss which shows pronounced peaks. The residue left is broadly frequency-independent or only weakly dependent over extended ranges of frequency which may be approximated by the limit $n \rightarrow 1$. Such a limit corresponds to frequency-independent components of the dielectric susceptibility, $\chi'(\omega)$ and $\chi''(\omega)$, with their ratio tending to infinity which is impossible practically but can be seen experimentally in various approximations. Figure 1 shows a compilation of data for different materials taken from much wider sets for different temperatures. These data are representative of a very wide range available in the published literature and are quoted here purely by way of examples. The data shown correspond to low or relatively low losses so that the real part of the permittivity $\epsilon'(\omega)$ does not vary by a large amount over the frequency range in question; and it is therefore possible to normalise the data by dividing $\chi''(\omega)$ by the corresponding $\epsilon'(\omega)$, thus defining the loss tangent $\tan \delta = \chi''(\omega)/\epsilon'(\omega)$, which gives absolute values of loss for the various samples while retaining the frequency dependence of $\chi''(\omega)$. The essential conclusion, coming from the analysis of the data presented in Figure 1, is that the residual loss follows in some cases law (5) while in other cases it is essentially “flat” in frequency with minor perturbations. It is interesting to note that the addition of 17% of carbon black to polyethylene causes a rise of $\tan \delta$

by one order of magnitude but hardly any change of the frequency dependence. It is also noteworthy that the total range of $\tan \delta$ covers at most three decades for materials for which the direct-current conductivity varies by many orders of magnitude. It is not profitable to fit these data to any particular law since they are the result of the interplay of minor accidental factors superimposed on the prevailing broad “flatness”. A theoretical justification for the existence of the fractional power law of type (5) with the exponent n arbitrarily close to unity would be sufficient for the understanding of all flat losses, any minor deviations being purely accidental.

In our theoretical approach to the analysis of the universal-response characteristics (5) we make use of the concept of dipolar screening introduced by Jonscher [23]. In the framework of this concept, the effectiveness of screening depends on the relative magnitudes of the thermally-activated-dipole density N_d with an energy W , $N_d \propto \exp(-W/kT)$, and the “critical” density $N_1 \propto kT/\mu^2$ where μ is the dipole moment of the dipole being screened. The theory of dipolar screening predicts that for low dipolar density, $N_d \ll N_1$, the number of dipoles within the field of any one dipole increases almost exponentially, so that their behaviour is strongly collective and the entire system behaves in the universal manner (5). On the other hand, for a high dipolar density, $N_d \gg N_1$, screening is effective, meaning that dipoles do not “see” their neighbours and behave individually in a Debye-like manner. This is summarized in Table 1. The situation is in many respects similar to the classical screening by charged particles but the onset of screening is much more rapid with a fall in the dipolar density N_d .

A considerable effort that has been devoted in the past to finding a theoretical explanation of the empirically observed results points on the two most widespread and at the same time least understood properties of the relaxation responses:

- the existence of the characteristic property (5) with its limiting form of virtually frequency-independent loss;
- the fact that this property of the relaxation responses is common to a very wide range of materials with very different physical and chemical interactions.

As a consequence, in theoretical attempts to model relaxation it has been commonly assumed that the empirical relaxation laws reflect a kind of general behaviour which is independent of the details of examined systems. This idea has stimulated the proposal of several relaxation mechanisms that differ mainly in the interpretation of the relaxation function. In recent attempts to find the origins of the non-Debye relaxation patterns the idea of complex systems as the “structures with variations” [24] that are characterised through a large diversity of elementary units and strong interactions between them is of special importance. The evolution in course of time of physical properties of a complex system is nonpredictable or anomalous [25], and the main feature of all the dynamical processes in such a system is their stochastic background. In the framework of statistical models (see e.g. [4-6, 8, 9, 11-14, 17-21, 26-31] the fact that the large scale behaviour of complex systems shows universality, i.e., that it is to some extent independent of the

precise local nature of the considered system, should come as no surprise. Intuitively, one expects “averaging principles” like the law of large numbers to be in force. However, it turns out to be very hard to make this intuition precise in concrete examples of stochastic systems with a large number of locally interacting components.

The empirical facts stress the need for a completely novel approach to the modelling of the dielectric relaxation and, to a certain extent, also mechanical relaxation, photoconduction, photoluminescence and chemical reaction kinetics (sharing some common features, see [15]). The need to understand the connections between the macroscopic property (5) of the relaxing complex system and the statistical properties of individual molecular or dipolar species requires the introduction into the relaxation theory of advanced methods of stochastic analysis. As shown by us [8, 32-34], a general formalism of limit theorems of probability theory plays an important role in constructing tools to relate the local random characteristics of the complex system to the empirical, deterministic relaxation laws, regardless of the specific nature of the system considered. The significance of the present paper lies in the fact that no one has clarified in a simple and plausible way, let alone one based on a stochastic argument, why the universal relation should exist at all and why the residual loss is such slowly variable function of frequency. Our approach provides a rigorous explanation for the most widely observed form of frequency dependence of the permittivity (or susceptibility) and thereby opens up a new and very powerful way of interpreting relaxation phenomena not only in the dielectric context.

The main objective of this paper is to focus on the approach to relaxation in the framework proposed in [33, 34] as consistent with Jonscher’s screening and energy criterion ideas and providing their strict mathematical formulation. We also bring to light the spatio-temporal scaling conditions hidden behind all the well-known empirical responses. For the reader’s convenience, the mathematical details necessary for the stochastic construction of the effective representation of a relaxing complex system are followed by extended comments.

In Section 2 we introduce the basic mathematical concept underlying the stochastic transition of a complex system from its initially imposed state. We show that the relaxational properties of the entire system can be represented by means of a random effective relaxation rate which contains information on the internal stochastic structure of the investigated system. In Section 3 we point to the origins of the statistical properties of the effective relaxation rate. We discuss the role of limit theorems of probability theory as the mathematical technique which allows us to derive the explicit relaxation formulas even with rather restricted information on local random properties of the system. In Section 4 we relate the statistical conditions yielding the well-known empirical responses to the spatio-temporal scaling properties of the relaxing complex system, and we show that they underlie Jonscher’s energy-criterion hypothesis. The last section contains conclusions.

2. Transition and survival probabilities

(i) Let us consider a complex physical system containing identical objects undergoing irreversible transitions from state A , imposed at time $t = 0$, to state B at random instants of time. States A and B differ in some physical parameter, so that the transition $A \rightarrow B$ is defined as the change of this particular parameter (changes in all other parameters may also have an influence on the transition). Let us choose one of the objects. Consider the conditional probability $p(t, dt)$ that this object will undergo the transition during the time interval $(t, t + dt)$ if the transition has not occurred before time t , i.e.

$$p(t, dt) = \Pr(t \leq \theta \leq t + dt | \theta \geq t) \quad (7)$$

where θ is the random waiting time for the transition of the chosen object. The conditional probability $p(t, dt)$ defined in (7) can be expressed in a form

$$p(t, dt) = -\frac{\Pr(\theta \geq t + dt) - \Pr(\theta \geq t)}{\Pr(\theta \geq t)}$$

where $\Pr(\theta \geq t + dt)$ and $\Pr(\theta \geq t)$ are the survival probabilities, i.e. the probabilities that the considered object will remain in state A until time $t + dt$ and t , respectively. The survival probability of the object can be expressed as

$$\Pr(\theta \geq t) = 1 - p(t)$$

where

$$p(t) = \Pr(\theta < t)$$

is the waiting time distribution of the object, i.e. the total probability of its transition $A \rightarrow B$ until time t . One can rewrite the survival probability in the form

$$\Pr(\theta \geq t) = \exp\left(-\int_0^t r(s) ds\right) \quad (8)$$

which is dependent on a non-negative quantity $r(s)$ called the intensity of transition [35]. This quantity is time-dependent, in general; and moreover, because of random impacts affecting each object, for different objects in the system it can take various values at the same instant of time [6].

The survival probability $\Pr(\theta \geq t)$ can be derived if one knows the explicit form of the intensity $r(s)$. For the time independent intensity $r(s) = b_0 = \text{const}$ one gets

$$\Pr(\theta \geq t) = \exp(-b_0 t)$$

what recovers the classical exponential evolutionary law for the object; the value b_0 determines the relaxation rate of the transition process. If, on the contrary, the intensity of transition is essentially time-dependent, then the evolutionary law for the object is of the

nonexponential form. In this case the resulting relaxation rate is not directly given by the intensity of transition as it is in the exponential case. In fact, taking into account the peculiarity of local random environment of an object, one should assume that, in general, the survival probability $\Pr(\theta \geq t)$ has the form of the weighted average of an exponential decay with respect to the probability distribution $F_\beta(b)$ of the relaxation rate of the object

$$\Pr(\theta \geq t) = \int_0^\infty e^{-bt} dF_\beta(b). \quad (9)$$

In other words, the relaxation rate of the object is the random variable β such that the total survival probability has the form

$$\Pr(\theta \geq t) = \langle \exp(-\beta t) \rangle \quad (10)$$

where the mean value $\langle \cdot \rangle$ is taken with respect to the relaxation-rate probability distribution $F_\beta(b)$. Expressions (9) and (10) are a generalisation of the Debye relaxation for which the relaxation rate β takes a constant value, say b_0 , with probability 1, $\Pr(\beta = b_0) = 1$. Then β has a degenerate probability distribution, $dF_\beta(b) = \delta(b - b_0)db$ (where $\delta(\cdot)$ denotes the Dirac delta function), and the integral on the right-hand side of (9) equals

$$\int_0^\infty e^{-bt} \delta(b - b_0) db = \exp(-b_0 t).$$

In general, in a complex system the probability distribution $F_\beta(b)$ and, consequently, the survival probability $\Pr(\theta \geq t)$ of an object are of unknown forms.

From equation (8) the intensity of transition from an initial state, $r(t)$, is related to the total survival probability $\Pr(\theta \geq t)$ of the object as follows

$$r(t) = -\frac{d}{dt} \ln \Pr(\theta \geq t). \quad (11)$$

Comparing (11) and (9) we obtain the relationship between the time-dependent intensity of transition and the relaxation rate distribution

$$r(t) = -\frac{d}{dt} \ln \int_0^\infty e^{-bt} dF_\beta(b).$$

The above mentioned lack of information about the relaxation rate distribution $F_\beta(b)$ yields that the corresponding intensity $r(t)$ is of unknown form. The explicit form of $r(t)$ depends on the characteristics of the random environment around the examined object and the rules needed to specify the sets of deterministic and stochastic parameters.

(ii) Consider (as before) a system of N objects, each waiting for transition $A \rightarrow B$ for some random time. For the i th object, $1 \leq i \leq N$, let the waiting time be denoted by θ_{iN} . The notation here (i.e. index “ iN ”) emphasizes the impact of the system size N on the behaviour of each individual object that has to be taken into account. The non-negative waiting times $\theta_{1N}, \dots, \theta_{NN}$ form a sequence of independent, identically distributed random variables. The waiting time distribution $p_{iN}(t) = \Pr(\theta_{iN} < t)$ is hence the same for each i and is equal to some function $F_\theta(t)$ that may depend on N .

The objects undergo transition in a certain order that can be reflected in the notion of order statistics [36] $\theta_{(1)} \leq \dots \leq \theta_{(N)}$, which is simply a nondecreasing rearrangement of times $\theta_{1N}, \dots, \theta_{NN}$. Traditionally, $\theta_{(l)}$ is called the l -th order statistics of sample $\theta_{1N}, \dots, \theta_{NN}$. Note that $\theta_{(1)} = \min(\theta_{1N}, \dots, \theta_{NN})$ and $\theta_{(N)} = \max(\theta_{1N}, \dots, \theta_{NN})$.

For a fixed size N of the system, the ratio of objects not transformed up to time t is equal to

$$1 - \frac{\eta_N(t)}{N} \quad (12)$$

where $\eta_N(t)$ denotes an unknown (random!) number of objects already transformed at time $t > 0$. For $l = 0, 1, \dots, N$ the events $\{\eta_N(t) = l\}$ that up to time t exactly l transitions occurred in the system can be expressed via order statistics in the following way:

$$\begin{aligned} \{\eta_N(t) = 0\} &= \{\theta_{(1)} > t\}, \\ \{\eta_N(t) = l\} &= \{\theta_{(l)} \leq t, \theta_{(l+1)} > t\} \quad \text{for } l = 1, \dots, N-1, \\ \{\eta_N(t) = N\} &= \{\theta_{(N)} \leq t\}, \end{aligned} \quad (13)$$

and the probability of such events is given by the Bernoulli model

$$\Pr(\eta_N(t) = l) = \binom{N}{l} [p_{iN}(t)]^l [1 - p_{iN}(t)]^{N-l}, \quad l = 0, 1, \dots, N. \quad (14)$$

Thus the random number $\eta_N(t)$ has the Bernoulli (binomial) distribution $\mathcal{B}(N, p)$ with parameter $p = p_{iN}(t)$. Consequently, the fraction in (12) is a random variable. However, it follows from the strong law of large numbers [37] that for N large enough

$$\frac{\eta_N(t)}{N} \approx \left\langle \frac{\eta_N(t)}{N} \right\rangle = p_{iN}(t) = F_\theta(t) \quad (15)$$

i.e. the random nature of the fraction in (12) vanishes for large N . Hence (12) is asymptotically equal to $(1 - p_{iN}(t))$ which is the survival probability $\Pr(\theta_{iN} \geq t)$ of any single object:

$$1 - \frac{\eta_N(t)}{N} \approx 1 - p_{iN}(t) = \Pr(\theta_{iN} \geq t). \quad (16)$$

The basic property of the relaxation function $\phi(t)$ is its monotonic decrease from 1 at $t = 0$ to 0 as $t \rightarrow \infty$. This is in fact a property of the survival probability and therefore (12) has been used as a definition of the relaxation function in several models.

Yet (12) can be used to describe the evolution of the entire system only if the behaviour of the system is represented by any individual object (from those forming the system). Unfortunately, this strict condition seems to contradict the idea of complexity of the investigated systems, and hence models defining the survival probability of a complex system as in (16) do not capture the nature of relaxation phenomena. Moreover, the relation (15) holds for any arbitrarily chosen form of the waiting time distribution (e.g. $F_\theta(t) = 0$ for $t < 0$, $= t$ for $0 \leq t \leq 1$, and $= 1$ for $t > 1$) so that the ratio in (15) is not uniquely determined. Therefore the attempts leaving the probabilistic analysis of the irreversible stochastic transitions in complex systems at this stage can only propose the form of distribution $F_\theta(t)$ fitting the data most exactly, see e.g. [6, 9]. They do not explain the observed fractional power law (5) indicating strictly limiting properties of the survival probability of the initial state of a complex system.

(iii) The considerations of irreversible stochastic transitions in complex systems show that the behaviour of the system as a whole, in general, cannot be attributed to any chosen object forming the system [6, 8, 9, 16]. Crucially relevant to this statement is the question of a proper mathematical construction of an “averaged” imaginary object representing the entire system. As it follows from (8), the intensity of transition from an initial state for any (real or imaginary) object depends on its survival probability. Let us denote the survival probability of an imaginary object representing the system as a whole by $\Pr(\tilde{\theta}_N \geq t)$ and by $\tilde{\theta}_N$ the effective waiting time for the entire system. Since the considered imaginary object represents the whole system, the survival probability $\Pr(\tilde{\theta}_N \geq t)$ is the probability that the transition of the system as a whole from its initial state (imposed by external constraints at $t = 0$) has not happened prior to a time instant t . This mathematical quantity is defined as the probability that there is no transition occurring in the system up to time t so that

$$\Pr(\tilde{\theta}_N \geq t) = \Pr(\eta_N(t) = 0).$$

By means of the Bernoulli scheme (14) with $l = 0$, the survival probability of the system is the product of N factors, each asymptotically equal to (12), see equation (16):

$$\Pr(\tilde{\theta}_N \geq t) = \Pr(\eta_N(t) = 0) = (1 - p_{iN}(t))^N.$$

On the other hand, by means of the order statistics $\{\eta_N(t) = 0\} = \{\theta_{(1)} \geq t\}$, see equation (13); and the survival probability of the entire system

$$\Pr(\tilde{\theta}_N \geq t) = \Pr(\eta_N(t) = 0) = \Pr(\theta_{(1)} \geq t) = \Pr(\min(\theta_{1N}, \dots, \theta_{NN}) \geq t)$$

is just the probability that the first passage of the system from the initial state has not happened before time t .

Since the waiting times $\theta_{1N}, \dots, \theta_{NN}$ are independent and identically distributed, we have

$$\Pr(\tilde{\theta}_N \geq t) = \Pr(\theta_{1N} \geq t) \dots \Pr(\theta_{NN} \geq t).$$

Assuming (10) for each θ_{iN} , i.e.

$$\Pr(\theta_{iN} \geq t) = \langle \exp(-\beta_{iN}t) \rangle$$

where random variables $\beta_{1N}, \dots, \beta_{NN}$ are also independent and identically distributed, we obtain that the survival probability of the system is of the form analogous to (10):

$$\Pr(\tilde{\theta}_N \geq t) = \langle \exp(-t\tilde{\beta}_N) \rangle \quad (17)$$

where

$$\tilde{\beta}_N = \sum_{i=1}^N \beta_{iN}. \quad (18)$$

The random variable $\tilde{\beta}_N$ can be considered as the effective relaxation rate representing the entire system; and, in accordance with the rate-theory concept (see e.g. [13]), individual relaxation rates β_{iN} 's are hence some contributions to the total rate $\tilde{\beta}_N$.

In fact, in any complex dielectric system under a weak external electric field only a part of the total number N of dipoles, referred to as “active” dipoles, is directly governed by changes of the field. The exact number of such dipoles depends on temperature, density of the dipolar species in the system, and interactions between them, and it is usually unknown. (In some cases it may take the value of the total number of the dipoles in the system.) Therefore, there can be only a part of dipoles contributing to the effective relaxation rate, and it is reasonable to modify formula (18) taking some unknown number ν_N instead of exactly N components:

$$\tilde{\beta}_N = \sum_{i=1}^{\nu_N} \beta_{iN}. \quad (19)$$

3. Origins of the random effective relaxation rate

The relaxation function $\phi(t)$, which is the probability that the initially imposed state of a macroscopic system survives by time t , is well known to be expressed as the weighted average of an exponential decay with respect to the distribution of the effective relaxation rate $\tilde{\beta}_N$ [13, 38, 39], and its explicit form depends on statistical properties of the rate. In view of (17), we can use the survival probability $\Pr(\tilde{\theta}_N \geq t)$ as a definition of the relaxation function and we obtain in this case that

$$\phi(t) = \langle \exp(-\tilde{\beta}_N t) \rangle \quad (20)$$

where $\tilde{\beta}_N$ is given by (19).

The evaluation of ν_N , the number of components in (19), which is in agreement with the nature of the relaxation phenomenon, has been presented in [33, 34]. It is based on the following idea:

Depending on the strength of screening, the active dipoles in the complex system may “see” each other to some extent. The collective behaviour of active dipoles results in the appearance of mesoscopic cooperative regions contributing to the macroscopic relaxation process [7, 15]. The number L_N of such mesoscopic regions in the system is determined by their sizes M_1, M_2, \dots and by the number of the active dipoles in the system [33].

The effective relaxation rate $\tilde{\beta}_N$ consists of the contributions $\overline{\beta_{jN}}$ of all L_N mesoscopic cooperative regions

$$\tilde{\beta}_N = \sum_{j=1}^{L_N} \overline{\beta_{jN}}. \quad (21)$$

Similarly, the relaxation rate $\overline{\beta_{jN}}$ of the j th mesoscopic region is the sum of the contributions β_{iN} of all active dipoles over the region [13, 32-34] and hence it is equal to

$$\overline{\beta_{jN}} = \sum_{i=M_1+\dots+M_{j-1}+1}^{M_1+\dots+M_j} \beta_{iN}. \quad (22)$$

As mentioned in section 2 (i), the individual relaxation rate, denoted here by β_{iN} , reflects the random intra-cluster dynamics, i.e. statistical properties of the interactions of the i th active dipole with some inactive neighbours forming around it a cluster of size N_i .

Comparing (19) and (21) with $\overline{\beta_{jN}}$ of the form (22) one obtains the explicit formula for ν_N , the number of the contributions to the total relaxation rate, in the framework of the proposed approach. For the sake of this paper it is not necessary to cite the entire complicated formula derived (for details see [33]). It is only important to note that ν_N is fully determined by N , the system size; by the cluster sizes N_1, N_2, \dots ; and by the cooperative-region sizes M_1, M_2, \dots . The number of the dipoles directly engaged in the relaxation process, their location, interaction range, relaxation rates, and all the quantities defined by them are random. Their precise stochastic characteristics determining the relaxation response of the system are unknown, unfortunately. However, as a rule, the relaxing systems consist of a large number of dipoles so that the distribution of $\tilde{\beta}_N$ can be satisfactorily approximated by the weak limit

$$\tilde{\beta} = \lim_{N \rightarrow \infty} \tilde{\beta}_N. \quad (23)$$

In practice, even $N \sim 10^6$ can suffice to replace adequately $\tilde{\beta}_N$ in (20) by the limit $\tilde{\beta}$.

On the basis of the limit theorems of probability theory the distribution of the effective relaxation rate $\tilde{\beta}$ in (23) and the resulting form of the relaxation response (20) in time or the corresponding susceptibility in frequency domain

$$\chi'(\omega) - i\chi''(\omega) \propto \phi^*(\omega) = \int_0^\infty e^{-i\omega t} \left(-\frac{d\phi}{dt}(t) \right) dt$$

can be derived even with rather restricted information on properties of the micro/mesoscopic statistical levels in the system. It appears [33, 34] that each of the well-known dielectric

responses can be obtained in this way if appropriate conditions are imposed on the basic random quantities: the cluster sizes N_i , the sizes M_j of the cooperative regions of correlated clusters, and the individual active-dipole relaxation rates β_{iN} .

4. Foundations of the universal response

Table 2 collects the statistical properties shown [33, 34] to underlie the KWW, HN, CC, CD, and Debye relaxation responses, given by formulas (3) and (4). As it follows from the table, the empirical responses are realized by various stochastic schemes. The conditions imposed on N_i , M_j , and β_{iN} here take one of two forms; either the distribution of the quantity considered is of finite mean value or it has a heavy tail. Let us explain that the distribution of a nonnegative random variable, say X , has a heavy tail if for some $0 < a < 1$ the tail function $\Pr(X > x) \sim x^{-a}$ for large x , i.e.,

$$\lim_{x \rightarrow \infty} \frac{\Pr(X > x)}{x^{-a}} = \text{const} > 0. \quad (24)$$

Classical example of the heavy-tailed distribution is the Pareto distribution [40]

$$\Pr(X > x) = \frac{1}{1 + (Ax)^c}, \quad x > 0$$

with the shape parameter $0 < c < 1$ and any positive scale constant A . (In this case the heavy-tail exponent $a = c$.) Another distribution possessing this property is a generalisation of the Pareto example; namely, the Burr law [40]

$$\Pr(X > x) = \frac{1}{(1 + (Ax)^c)^d}, \quad x > 0$$

with the shape parameters $c, d > 0$ such that $0 < cd < 1$ and any positive scale constant A . (Here the heavy-tail exponent $a = cd$.) More difficult but interesting heavy-tailed distributions are the completely asymmetric Lévy-stable laws [36] defined by their Laplace transforms $\mathcal{L}(X; t) = \exp(-(At)^c)$ with $0 < c < 1$ and $A > 0$. (In this case the heavy-tail exponent $a = c$.)

Condition (24) applied to any random variable X expresses the following scaling property of the magnitude represented by X :

$$\Pr(X \geq Cx) \approx C^{-a} \Pr(X \geq x), \quad x \rightarrow \infty, \quad (25)$$

for any fixed constant $C > 0$. (If there exists the corresponding probability density $w(x)$, the condition (25) yields $w(Cx) \sim C^{-a-1}w(x)$ for large x .) Hence, in the presented approach the heavy-tail property is directly related to the spatial (if referred to N_i and M_j , the cluster and the cooperative-region sizes) or temporal (if referred to the relaxation rate β_{iN}) scaling properties of the system. Comparing the non-Debye responses with the

Debye one, as done in Table 3, one can see that the difference between them lies in the presence of such a scaling in the system. Namely, in the Debye case, that of the individual behaviour of the active dipoles, there is no property of this form. By contrast, spatial or/and temporal scaling can be found for other responses. Moreover, at least one of the two variates M_j and β_{iN} has a heavy-tailed distribution in the non-Debye cases. Since, as equation (22) shows, the correlated-cluster relaxation rate $\overline{\beta_{jN}}$ includes both those quantities; its distribution has also a heavy tail, “producing” a hierarchy of mesoscopic relaxation rates; i.e. the same proportion of smaller or larger mesoscopic contributions to the effective response no matter the scale at which one is looking at the relaxation rate distribution. This property follows from both the stochastic properties of the active dipoles generated by the intra-cluster dynamics and the strength of screening yielding the range of interactions between them.

As a consequence of the proposed approach, the origins of the macroscopic energy criterion coefficient can be pointed out. As we have already explained, the heavy-tailed distribution of any (micro/meso/macroscopic) relaxation rate β reflects the scaling property of the rate

$$\Pr(\beta \geq Cb) \approx C^{-a} \Pr(\beta \geq b), \quad b \rightarrow \infty, \quad (26)$$

for any fixed constant $C > 0$ (where a is the heavy-tail exponent). As in (10) and (17), we have $\Pr(\theta \geq t) = \langle \exp(-\beta t) \rangle$ so that the properties of the micro/meso/macroscopic relaxation rates determine the survival probabilities of the microscopic (active dipole), mesoscopic (cooperative region), and macroscopic (entire system) objects, respectively; thus, by analogy to (20), defining the function $\phi(t) = \langle \exp(-\beta t) \rangle$, for simplicity referred to as the micro/meso/macroscopic relaxation function.

The asymptotic behavior (26) of the relaxation-rate distribution at large b is connected with the short-time behavior of the associated relaxation function $\phi(t)$ [36]. Namely, at the origin $t \rightarrow 0$ the response function $f(t) = -\frac{d\phi(t)}{dt}$ takes the form

$$f(t) \propto t^{a-1} L(t) \quad (27)$$

where $L(t)$ is a function slowly varying at $t = 0$ (i.e., $L(Ct)/L(t) \rightarrow 1$ as $t \rightarrow 0$ for any fixed positive constant C). Then, it can be shown [41] that the short-time property (27) of the response function $f(t)$ corresponds to the following asymptotic behavior of $\chi(\omega) \propto \phi^*(\omega) = \int_0^\infty e^{-i\omega t} f(t) dt$ for the high-frequency region:

$$\chi(\omega) = \chi'(\omega) - i\chi''(\omega) \propto (i\omega)^{-a} L(1/\omega) \quad \text{for } \omega \rightarrow \infty. \quad (28)$$

Property (28) leads straightforwardly to the constant ratio

$$\frac{\chi''(\omega)}{\chi'(\omega)} = \cot\left(\eta \frac{\pi}{2}\right) \quad \text{for } \omega \gg \omega_p$$

with $\eta = 1 - a$. This result, interpreted as the (micro/meso/macroscopic) energy criterion, is consistent with the energy criterion (6) if only η is equal to the macroscopic high-frequency power-law exponent n . Summing up, the heavy-tail property of the relaxation rate with the heavy-tail exponent a leads to the energy criterion with the characteristic constant $\eta = 1 - a$.

Table 4 contains the detailed discussion of the energy criterion at the micro/meso/macroscopic levels for the cases related to the KWW, HN, CC and CD empirical relaxation responses (3) and (4). Observe that in each particular response the parameter η followed from the mesoscopic-relaxation-rate tail is equal to the macroscopic energy-criterion coefficient n , and hence, that the high-frequency universal laws (5) and (6) and its parameter n are determined by the heavy-tail properties of the mesoscopic (correlated-cluster) relaxation rate distributions. The above proves Jonscher's hypothesis introduced in his screening theory of relaxation and stating that in order to observe property (6) at the macroscopic level, the same property must characterise the behaviour of the relaxing dipoles. As shown in Table 4, in general, the energy-criterion parameter agrees with n from equation (6) on the mesoscopic level, only.

5. Conclusions

To our knowledge, this is the first attempt to relate rigorously the widely observed universal macroscopic laws to the micro/mesoscopic statistical characteristics of the complex system, thereby establishing a basis for the understanding of the stochastic origins of the relaxation phenomenon. The essential element which was required for the derivation of these results is the strict probabilistic formalism in terms of which the dipolar screening and energy criterion concepts can be expressed.

In terms of our analysis, the conditions for the universal relaxation response may be stated as follows:

- (i) at the microscopic level, a random number of the active dipoles, those that follow changes of the external field, is selected; their individual relaxation rates are determined by the interactions of the active dipoles with inactive neighbours forming random-sized clusters around them;
- (ii) at the mesoscopic level, correlated-cluster regions of sizes depending on the strength of screening appear; the collective rate of relaxation of the active dipoles in such a mesoscopic cooperative region becomes correlated with the number of the active dipoles in the region and with the stochastic properties of their individual relaxation rates, see equation (22); the mesoscopic correlated-cluster relaxation rate combines both the spatial and the temporal scaling properties of the system;
- (iii) at the macroscopic level, averaging over the number of effective contributions and their rates leads to the universal relaxation for the entire system, giving law (5); the

sufficient condition of this is that the high-frequency energy criterion is satisfied at the mesoscopic level; the mesoscopic energy criterion is provided by the heavy-tail property of the correlated-cluster relaxation rates.

References

- [1] A.K. Jonscher, *Nature* 267 (1977) 673.
- [2] C.J. Böttcher, and P. Bordewijk, *Theory of Electronic Polarisation* vol. 2, Elsevier, Amsterdam, 1978.
- [3] A.K. Jonscher, *Dielectric Relaxation in Solids*, Chelsea Dielectrics Press, London, 1983.
- [4] R.V. Chamberlin and D.N. Haines, *Phys. Rev. Lett.* 65 (1990) 2197.
- [5] K.L. Ngai, R.W. Rendell and D.J. Plazek, *J. Chem. Phys.* 94 (1991) 3018.
- [6] Yu.A. Berlin, D.O. Drobnitsky, V.V. and Kuz'min, *J. Phys. A: Math. Gen.* 26 (1993) 5973.
- [7] A.K. Jonscher, *Applied Physics A* 56 (1993) 405.
- [8] K. Weron and A. Jurlewicz, *J. Phys. A: Math. Gen.* 26 (1993) 395.
- [9] Yu.A. Berlin, D.O. Drobnitsky, V.V. and Kuz'min, *J. Chem. Phys.* 100 (1994) 3163.
- [10] S. Havriliak Jr. and S.J. Havriliak, *J. Non-Cryst. Solids* 172-174 (1994) 297.
- [11] V. Halpern, *J. Phys.: Condens. Matter* 7 (1995) 7687.
- [12] I. Koponen, *J. Non-Cryst. Solids* 189 (1995) 154.
- [13] M.O. Vlad and M.C. Mackey, *J. Math. Phys.* 36 (1995) 1834.
- [14] R.V. Chamberlin, *Europhys. Lett.* 33 (1996) 545.
- [15] A.K. Jonscher, *Universal Relaxation Law*, Chelsea Dielectrics Press, London, 1996.
- [16] K. Weron and M. Kotulski, *J. Stat. Phys.* 88 (1997) 1241.
- [17] R. Metzler, E. Barkai and J. Klafter, *Phys. Rev. Lett.* 82 (1999) 3563.
- [18] R. Metzler and J. Klafter, *Phys. Rep.* 339 (2000) 1.
- [19] V.I. Arkhipov, *J. Non-Cryst. Solids* 305 (2002) 127.
- [20] A. Blumen, A.A. Gurtovenko, S.Jespersen, *J. Non-Cryst. Solids* 305 (2002) 71.

- [21] R. Metzler and J. Klafter, J. Non-Cryst. Solids 305 (2002) 81.
- [22] A.K. Jonscher, IEEE Trans. on Dielectrics and EI, vol. 8 (2001) 345.
- [23] A.K. Jonscher, J. Material Sci. 32 (1997) 6409.
- [24] N. Goldenfeld and L.P. Kadanoff, Science 284 (1999) 87.
- [25] F. Guerra, L. Peliti, A. Vulpiani, in L. Peliti, A. Vulpiani (Eds.), *Measures of Complexity*, Springer, Berlin, 1988.
- [26] M.I. Dykman, D.G. Luchinsky, R. Mannella, P.V.E. McClintock, N.D. Stein, and N.G. Stocks, Nuovo Cimento D 17 (1995) 661.
- [27] A. Fuliński, Phys. Rev. E 52 (1995) 4523.
- [28] L. Gamaitoni, P. Hänggi, P. Jung, and F. Marchesoni, Rev. Mod. Phys. 70 (1998) 223.
- [29] A. Weron, Sz. Mercik, and R. Weron, Physica A 264 (1999) 562.
- [30] Sz. Mercik and R. Weron, Physica A 267 (1999) 239.
- [31] Sz. Mercik and K. Weron, Phys. Rev. E 63 (2001) 051910.
- [32] A. Jurlewicz and K. Weron, Cell. Molec. Biol. Lett. 4 (1999) 55.
- [33] K. Weron, A. Jurlewicz, and A.K. Jonscher, IEEE Trans. Dielectrics and E.I. Vol. 8, No. 3, (2001) 352.
- [34] A. Jurlewicz and K. Weron, J. Non-Cryst. Solids 305 (2002) 112.
- [35] N.G. Van Kampen, *Stochastic Processes in Physics and Chemistry*, Elsevier, Amsterdam, 1987.
- [36] W. Feller, *An Introduction to Probability Theory and Its Applications*, Vol. 1 and 2, Wiley, New York, 1966.
- [37] Y. Viniotis, *Probability and Random Processes for Electrical Engineers*, McGraw-Hill, Boston, 1998.
- [38] J. Klafter and M.F. Shlesinger, Proc. Natl. Acad. Sci. USA, 83 (1986) 848.
- [39] M.R. de la Fuente, M.A. Perez Jubindo, J.D. Solier and M.J. Tello, Phys. Rev. B 37 (1988) 2094.
- [40] N.L. Johnson and S. Kotz, *Distributions in Statistics: Discrete Distributions; Distributions in Statistics: Continuous Univariate Distributions 1, 2*, Wiley, New York, 1969, 1970.

- [41] A.I. Saichev and W.A. Woyczynski, *Distributions in the Physical and Engineering Sciences*, Birkhäuser, Boston, 1997.

Table 1.
Dipolar screening schemes.

Table 1

Condition	Screening	Physical picture	Consequences	
$N_d \gg N_1$	effective	Dipoles do not "see" one another	Individual behavior	Debye-like response
$N_d \ll N_1$	ineffective	Dipoles interact strongly	Collective behavior	Universal response

Table 2.

Stochastic origins of the empirical relaxation responses.

Table 2

Conditions for:			Relaxation response	Energy-criterion parameter
active-dipole relaxation rate β_{iN}	cluster size N_i	cooperative -region size M_j		$0 < n < 1$
heavy tail with $a = \alpha$	heavy tail with $a = \alpha$	heavy tail with $a = \gamma$	HN $0 < \alpha < 1$ $0 < \gamma < 1$	$n = 1 - \alpha\gamma$
heavy tail with $a = \alpha$	heavy tail with $a = \alpha$	$\langle M_j \rangle < \infty$	CC $0 < \alpha < 1$ $\gamma = 1$	$n = 1 - \alpha$
$\langle \beta_{iN} \rangle < \infty$	$\langle N_i \rangle < \infty$	heavy tail with $a = \gamma$	CD $\alpha = 1$ $0 < \gamma < 1$	$n = 1 - \gamma$
heavy tail with $a = \alpha$	$\langle N_i \rangle < \infty$	$\langle M_j \rangle < \infty$	KWW $0 < \alpha < 1$	$n = 1 - \alpha$
$\langle \beta_{iN} \rangle < \infty$	$\langle N_i \rangle < \infty$	$\langle M_j \rangle < \infty$	Debye $\alpha = 1$ $\gamma = 1$	energy criterion not fulfilled

Table 3.

Comparison of the non-Debye relaxation responses to the Debye one.

Table 3

Non-Debye responses (collective behavior of the dipoles):	Debye response (individual behavior of the dipoles):
<p>The relaxation rates of the dipoles responding to changes of the external electric field,</p> <p style="text-align: center;">or</p> <p>the cluster sizes,</p> <p style="text-align: center;">or</p> <p>the sizes of correlated-cluster regions</p> <p>have heavy-tailed distributions, and, as a result, infinite expected values.</p> <hr/> <p>(Note that the HN response is the only case in which all three distributions have heavy tails.)</p>	<p>The relaxation rates of the dipoles responding to changes of the external electric field,</p> <p style="text-align: center;">and</p> <p>the cluster sizes,</p> <p style="text-align: center;">and</p> <p>the sizes of correlated-cluster regions (if any)</p> <p>have distributions with finite mean values.</p> <hr/> <p>(Note that <i>the dipoles do not have to respond with the same rate</i> but the rates are of limited distribution.)</p>
Spatial and/or temporal scaling is present at the different statistical levels of the system.	Neither spatial nor temporal scaling appears at any level.

Table 4.

Discussion of the energy criterion at the micro/meso/macrosopic levels.

Table 4

Universal response	Relaxation rate			$\chi''(\omega)/\chi'(\omega) = \cot (\eta\pi/2)$		
	β_{iN} (micro)	$\overline{\beta_{jN}}$ (meso)	$\tilde{\beta}$ (macro)	micro	meso	macro
HN	heavy tail with $a=\alpha$	heavy tail with $a=\alpha\gamma$	heavy tail with $a=\alpha\gamma$	$\eta = 1-\alpha \neq n$	$\eta = 1-\alpha\gamma = n$	
CC KWW	heavy tail with $a=\alpha$	heavy tail with $a=\alpha$	heavy tail with $a=\alpha$	$\eta = 1-\alpha = n$		
CD	$\langle\beta_{iN}\rangle < \infty$	heavy tail with $a=\gamma$	heavy tail with $a=\gamma$	does not hold	$\eta = 1-\gamma = n$	

Figure captions

Figure 1.

Typical examples of the frequency dependence of the residual loss, after subtraction of dc component, low-frequency dispersion and strong dipolar peaks, plotted logarithmically against frequency, for a range of dielectric materials. The data cover more than ten decades of frequency, and the prevailing trend is a “flat” or frequency-independent loss with only minor deviations, for instance the slope -0.2 over six decades for pure polyethylene. The $\tan \delta$ values cover a range of barely three decades between the lowest and highest losses; and the surprising feature is the very slight effect of the addition of conducting species (like 12% graphite to polyethylene raising the loss by a factor of 3, and 17% of graphite by a further factor of 3) with very little change of the frequency dependence. Likewise, the addition of 55% of graphite to boron nitride does not raise the extremely low loss of the system. Most of the data quoted here are taken from much wider ranges for variable temperature and for ranges of composition. The evident trends are the general “flatness” of the losses in frequency which is not compatible with any known mechanism and that irrespective of the absolute level of loss. Detailed information: $\text{Pb}_2\text{Sc}_{0.9}\text{Ta}_{0.9}\text{Ti}_{0.1}\text{O}_6$ and $\text{Pb}_2\text{ScTaO}_6$ are ferroelectric ceramics, from A. Isnin and A.K. Jonscher, *Ferroelectrics*, 210 (1998) 47. Pure polyethylene (PE) showing nine decades of frequency with a very slowly varying $\tan \delta$ in the range 3×10^{-4} - 2×10^{-3} with a frequency dependence proportional to $f^{-0.2}$ over most of the middle range; also shown are data for polyethylene with admixtures of 12% and 17% of graphite; from D.S. McLachlan and M.B. Heaney, *Phys. Rev. B* 60 (1999) 12746. Single crystal CaTiO_3 over a range of temperatures with $\tan \delta = 5 - 9 \times 10^{-4}$, show extremely small values of $1-n = 0.000325$ to 0.000625 ; from B.S. Lim, A.V. Vaysleyb, and A.S. Nowick, *Applied Physics A* 56 (1993) 8. Alpha-poly-vinylidene di-fluoride ($\text{PVDF}\alpha$) data from A.K. Jonscher and G. Menegotto, *IEEE Trans. Dielectrics and EI* 7 (2000) 303. Percolation system graphite-boron nitride (45%BN+55%C) from J.J. Wu and D.S. McLachlan, *Phys. Rev. B* 56 (1997) 1236; *Phys. Rev. B* 58 (1998) 14880. Zeolite plus NLO-active para-aniline from M. Wuebbenhorst, private communication.

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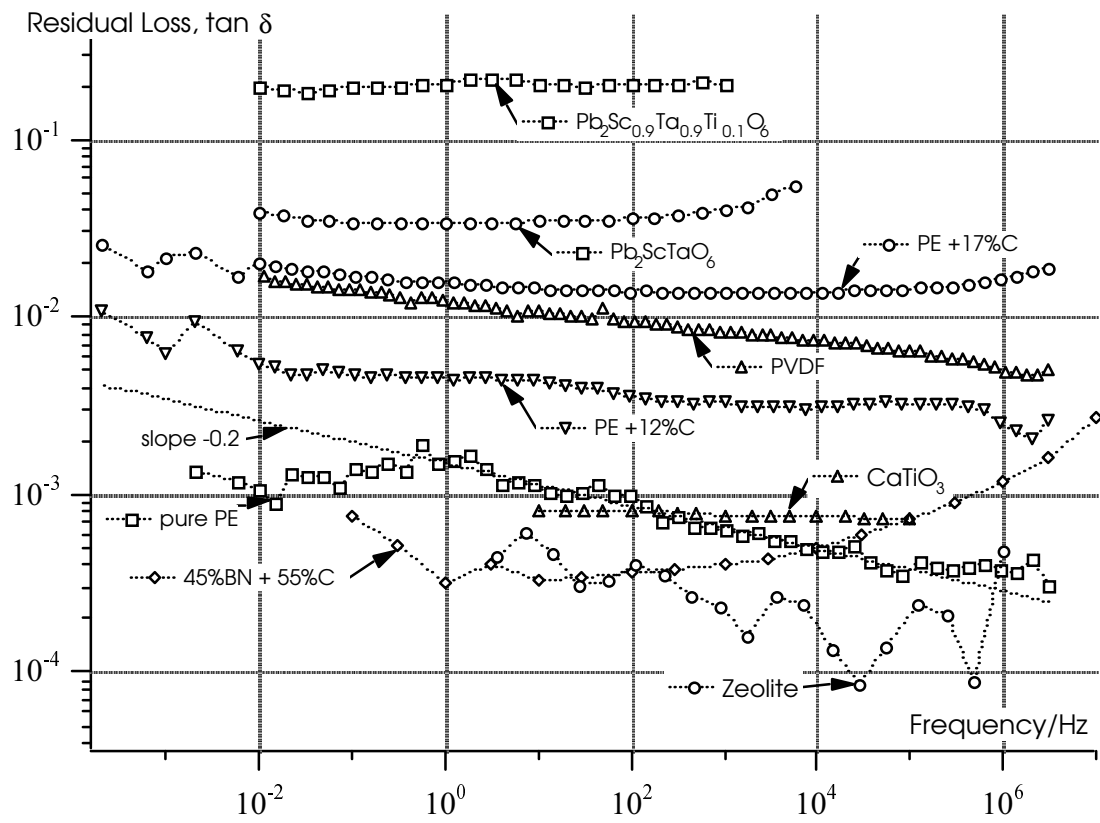


Figure 1